

OPP OFFICIAL RECORD
HEALTH EFFECTS DIVISION
SCIENTIFIC DATA REVIEWS



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

APR 23 1992

OFFICE OF
PESTICIDES AND TOXIC
SUBSTANCES

MEMORANDUM

SUBJECT: PP0F3872. Pinnacle® (thifensulfuron methyl) on corn. Evaluation of Analytical Methods and Residue Data. CBTS No. 7173, 7174. Bar Code D156732. Mrid 41542201, 41542202, 41542203, 41561801, 41561802.

FROM: R. W. Cook, Chemist
Tolerance Petition Section I
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Health Effects Division (H7509C)

THRU: Debra Edwards, Ph.D., Acting Chief
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and

Toxicology Branch
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Health Effects Division (H7509C)

The petitioner, Du Pont Agricultural Products, Wilmington, Delaware, proposes tolerances for residues of the herbicide thifensulfuron {methyl 3-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylate} in or on the raw agricultural commodities field corn forage and fodder at 0.1 ppm and in or on field corn grain at 0.05 ppm. The product name is Pinnacle® Herbicide. The active ingredient is also known by the company designation DPX-M6316 and is the active ingredient in Harmony® Herbicide.

Tolerances are established under 40 CFR 180.439 for residues of thifensulfuron methyl on soybeans, barley straw, wheat straw at 0.1 ppm and in wheat grain and barley grain at 0.05 ppm. These tolerances were established under PP6F3431 and PP8F3663 (Du Pont Harmony® Herbicide EPA Reg No. 352-446). Temporary tolerances for residues of DPX-M6316 in or on soybeans have been established under PP8G3602 (Pinnacle® Herbicide EPA Experimental Use Permit 352-EUP-145). In addition, emergency exemptions under

- 2 -

Section 18 were considered under 87-VA-01 and 87-VA-02 (see M. Metzger, 1/27/87) for wheat and barley and in 89-LA-01 (see F. Suhre, 2/3/89) for oats.

A "new chemical" registration standard has been issued for Harmony® (DPX-M6316) which is now known by the common name thifensulfuron methyl. See registration standard dated 2/12/87 in this regard.

Conclusions

1. The nature of the residue resulting from the application of thifensulfuron methyl to field corn is adequately understood. The residue of concern in plants is the parent compound per se.

In animals, the nature of the residue resulting from the application of thifensulfuron methyl to growing crops is adequately understood. The residue of concern in animals is thifensulfuron methyl per se.

2. The intended application rate is as stated in Section B of PP0F3872, i.e. 0.25 oz./A. of the product Pinnacle® Herbicide, equivalent to 0.0625 oz. a.i. thifensulfuron methyl per acre. The petitioner should clarify that the label rate is correct and not the 0.25 oz. active per acre stated on page 7, ID AMR-1233-88.
3. There is an adequate enforcement method for residues of thifensulfuron methyl. The method has been forwarded to FDA for inclusion in PAM II.
4. Provided the petitioner verifies the application rate per Conclusion 2 above, we conclude that residues of thifensulfuron methyl are not likely to exceed the proposed tolerances of 0.02 ppm in corn grain and 0.05 ppm in corn forage and corn fodder, when used in a single application at no more than the proposed label rate of 0.0625 oz a.i./A. with a preharvest interval of 30 days prior to harvest of corn forage or fodder.
5. Provided the petitioner verifies the application rate per Conclusion 2 above, in the absence of detectable residues in corn milling fractions, we are not requiring food/feed additive tolerances for corn meal or corn oil. If the petitioner should propose a future use which results in detectable residues in corn grain, food/feed tolerances may then be required for secondary residues in processed commodities.
6. Provided the petitioner verifies the application rate per Conclusion 2 above, in the absence of detectable residues in animal feed items corn grain, forage or fodder, we are not requiring tolerances for meat, milk, poultry or eggs at this time. If the petitioner should propose a future use which results in detectable residues in animal

- 3 -

feed items, feeding studies and tolerances may be required for secondary residues in meat, milk, poultry, and eggs.

7. An International Residue Limit Status Sheet (Codex) is attached to our review.

Recommendations

Provided the petitioner verifies the application rate per conclusion 2 above, we recommend for the establishment of the proposed tolerances for residues of thifensulfuron methyl in corn grain at 0.02 ppm, and in corn forage and fodder at 0.05 ppm.

DETAILED CONSIDERATIONS

Manufacture and Formulation

The manufacturing process is discussed in the product chemistry submission previously submitted by the petitioner. The product chemistry data has been reviewed by Registration Division.

The plant regulating product Pinnacle® is formulated as a granular material intended to be dissolved in water for application by ground equipment.

Directions for Use

Pinnacle® Herbicide 25 DF on field corn:

The label directions for use are to apply 1/4 ounce Pinnacle® per acre (0.062 ounces a.i./A). Apply by ground equipment only. Do not apply by air. Use a minimum of 10 gallons of water per acre for ground application. Pinnacle® can be applied to 2-6 leaf corn. Do not graze or feed forage or grain from treated area to livestock within 30 days of application.

Do not apply to corn previously treated with Counter insecticide applied at planting or over-the-row at cultivation as severe crop injury may result.

Include a surfactant at the rate of 0.125% v/v (1 pint per 100 gallons of spray solution). Use a non-ionic surfactant of at least 80% active ingredient. The addition of liquid nitrogen fertilizer at the rate (concentration) of 4% v/v (4 gallon per 100 gallons of spray solution) is required for control of certain species. Under dry conditions a non-ionic surfactant of 0.25% v/v (2 pints per 100 gallons of spray solution) or crop oil concentrate at 0.5% v/v (4 pints per 100 gallons of spray solution)

- 4 -

We note a discrepancy between the label directed rate of 0.25 ounce of Pinnacle® (0.062 ounces active ingredient per acre) in Section B (label) of PP0F3872 submitted 4/26/90 and page 7 of Du Pont laboratory project ID AMR-1233-88 which states that the proposed label recommends a single application at rates from 0.062 to 0.25 ounces active ingredient equivalent to 0.25 to 1.0 ounces of product per acre. The petitioner should clarify the intended application rate.

Nature of the Residue

The nature of the residue in wheat and barley grain and straw has been previously discussed in the Harmony® registration standard. It was concluded that the nature of the residue was not adequately known for the purposes of the standard. The petitioner later responded and upon further review it was concluded that the nature of the residue in wheat and barley was adequate for the establishment of tolerances on these commodities.

The petitioner has submitted additional nature of the residue study for thifensulfuron methyl in corn. The study is named Du Pont Report No. AMR-532-86, "METABOLISM OF [THIOPHENE-2-¹⁴C] DPX-M6316 AND [TRIAZINE-2-¹⁴C] DPX-M6316 IN FIELD GROWN CORN" by V. A Wittenbach. Small field plots were treated with 35 g/ha (0.03 lb a.i./A.) of either [thiophene-2-¹⁴C] DPX-M6316 or [triazine-2-¹⁴C] DPX-M6316 formulated similarly to the herbicide product Harmony®. Corn plants of the Pioneer 3378 variety were treated at 20 days, in the fourth leaf stage, as specified in the proposed use directions. Plant samples were collected at 0, 3, 10, 30, 72, and 113 days after the application of [thiophene-2-¹⁴C] DPX-M6316 and [triazine-2-¹⁴C] DPX-M6316. At the 113 day sampling interval, corn grain was collected separately from the remainder of the plant. After transport to laboratory and weighing, the samples were frozen and stored at -20°C. Samples obtained at 0, 3, and 10 days were washed with acetone:water 80:20 prior to freezing. The wash water was retained for analysis to determine surface residues.

Homogenized samples were extracted with acetone:water, the supernatant transferred into aqueous phase at pH 7.5 and quantitatively transferred into acetonitrile for HPLC and radiometry. Samples from the 30+ days after treatment were extracted with hexane prior to taking the water phase to dryness. Solid materials after the acetone extraction were further extracted with ammonium carbonate with EDTA to remove additional ¹⁴C. Aliquots of homogenized samples, retained pellets, etc, were also combusted for total radioactivity. Radioassay involved liquid scintillation counting by appropriate equipment.

Results:

Corn Grain:

The amount of the radiolabel present in corn grain at the 113 day harvest was 0.0043 ppm for thiophene radiolabel and 0.0006 ppm for the triazine radiolabel. The amount of the radiolabel present in corn grain was too low for identification of the nature of the residue.

- 5 -

Corn Foliage:

When the nature of the [thiophene-2-¹⁴C] residue in corn foliage was examined as discussed above, residues of [thiophene-2-¹⁴C] DPX-M6316 declined rapidly through the first 30 days and were <0.01 ppm at Day 30 or longer intervals. The only metabolite detected was 2-acid-3-sulfonamide [3-(aminosulfonyl)-2-thiophene carboxylic acid] at <0.02 ppm at all intervals, and unextracted (by acetone:water) radiolabel showed maximum of 0.079 ppm at Day 3, declining over time to 0.0071 ppm at Day 113.

In considering the [triazine-2-¹⁴C] radiolabel, the same rapid decline of DPX-M6316 is shown, with no radiolabel present as [triazine-2-¹⁴C] DPX-M6316 after 30 days. Metabolites include:

- triazine urea [4-methoxy-6-methyl-1,3,5-triazinyl-2-urea]
- triazine amine [4-methoxy-6-methyl-1,3,5-triazine-2-amine]
- O-demethyl triazine urea [N-(4-hydroxy-6-methyl-1,3,5-triazine)urea]
- O-demethyl triazine amine [4-amino-6-methyl-1,3,5-triazine-2-ol]

All these metabolites were <0.02 at days 3 and 10 and much less at the longer intervals. Residues of radiolabel at Day 30 and longer intervals were <0.001 ppm for each of the detectable [triazine-2-¹⁴C] metabolites. This study shows similar metabolic pathways as shown in the previously submitted studies for wheat and barley. We conclude that the nature of the residue in corn foliage is adequately known and the residue of concern is the parent compound per se.

[Thiophene-2-¹⁴C] DPX-M6316 and [Triazine-2-¹⁴C] DPX-M6316 In Corn Foliage

[Thiophene-2- ¹⁴ C] DPX-M6316					[Triazine-2- ¹⁴ C] DPX-M6316			
Days	Fresh Weight	Growth Stage	% Day 0	PPM	Fresh Weight	Growth Stage	% Day 0	PPM
0	2.10	4th Leaf	100	1.467	2.40	4th Leaf	100	1.880
3	2.81	5th Leaf	76	0.8357	2.81	5th Leaf	56	0.8957
10	9.15	6th Leaf	49	0.1665	10.58	6th Leaf	41	0.1728
30	132.4	10th Leaf	36	0.0084	222.4	10th Leaf	13	0.0026
72	402.1	Forage Stage	126	0.0096	428.1	Forage Stage	4	0.0005
113	337.7	Final Harvest	192	0.0174	341.9	Final Harvest	13	0.0016
113 Grain	135.4	Harvest Grain	—	0.0043	144.7	Harvest Grain	—	0.0006

From Tables 2, 3, and 4

Nature of the Residue in Animals

- 6 -

There is an animal metabolism study (lactating goat) reviewed by C. Deyrup in PP6F3431. Lactating goats were fed 50 mg DPX-M6316, equivalent to 28 ppm in the daily diet for 7 days.

In brief, the results showed no detectable levels of either [thiophene-2-¹⁴C] DPX-M6316 or [triazine-2-¹⁴C] DPX-M6316 equivalents in fat or heart tissue of goats. Residues of [thiophene-2-¹⁴C] DPX-M6316 and [triazine-2-¹⁴C] DPX-M6316 equivalents in other organs ranged from no detectable residue to 0.16 ppm. Residues of both radiolabels in milk ranged up to 0.16 ppm

The ¹⁴C materials found in the [thiophene-2-¹⁴C] DPX-M6316 goat study included DPX-M6316, DPX-M6316 acid, O-demethyl-DPX-M6316, thiophene sulfonimide, 2-acid-sulfonamide, 2-ester-3-sulfonamide, unknown metabolite M2 and other unidentified ¹⁴C materials. In milk, 72 to 88% of the ¹⁴C was identified. The ¹⁴C materials found in the [triazine-2-¹⁴C] DPX-M6316 goat study included DPX-M6316, DPX-M6316 acid, O-demethyl-DPX-M6316, O-demethyl triazine amine, triazine amine, unknown metabolite M1 and other unidentified ¹⁴C materials. In milk, a total of 84 to 90% of the ¹⁴C was identified.

Based upon the goat metabolism study with 2800 x feeding level exaggeration and upon the no detectable levels of thifensulfuron methyl residues in corn grain, corn forage or fodder from exaggerated application rates (see below under Residue Data), we can conclude that the nature of the residue is adequately understood for the purposes of establishing the proposed tolerance on corn grain, forage, and fodder. We conclude that metabolism studies in poultry are not needed at this time. However, if the petitioner should propose a use which results in significant levels of residues of concern in poultry feed, poultry metabolism studies would be needed.

Analytical Method

Analysis of corn kernels, ears, and green forage.

Du Pont Study No. AMR 431-85 Revision 3 August 11, 1988 MRID415422O2.

The method involves soaking in pH 3 water followed by ethyl acetate extraction. It was used for residue data on corn kernels, whole ears, and green forage. This method differs from Du Pont Study No. AMR 410-85 which extracts with ethyl acetate without soaking. In brief, in the method of Du Pont Report No. AMR 431-85, 25 grams of kernels or 10 grams of green forage or whole ears were soaked in 25 ml of aqueous sodium bicarbonate and 75 ml of ethyl acetate. The pH was adjusted to 3.0 by dropwise addition of hydrochloric acid. The sample was extracted for 2 minutes in a Tekmar Tissumizer®. The sample was centrifuged at 2500 rpm for 10 minutes and liquid layer decanted. The extraction steps were repeated three more times and the resulting liquid layers combined.

- 7 -

For kernels, the combined solution was partitioned three times with 100 ml of aqueous 0.1 M sodium bicarbonate. The aqueous layer was dropwise acidified to pH 3.5 with 1.0 N HCl. The next step of the procedure must occur within one hour.

For green forage and whole ears, the ethyl acetate solution is partitioned three times with aqueous sodium bicarbonate and the aqueous layer retained, and extracted three times with hexane (discarded). The solution is acidified as above, and the procedure continued within the hour.

At this point, the samples are quantitatively transferred to methylene chloride which is evaporated to 4-5 ml on a rotary evaporator and then taken to dryness under a stream of nitrogen. Samples are then stored under freezer conditions until analysis. Samples are filtered through Millipore® Millex® prior to analysis in a Du Pont Model 8800 Liquid Chromatograph with a Tracor® Model 965 photoconductivity detector.

Recoveries of DPX-M6316 from Corn Fractions ¹

Crop	Fortification, ppb	Replicates	Mean, %	Range, %
Kernels	20	6	88	76-100
	50	6	93	81-100
	200	6	98	88-111
Green forage	50	6	85	71-95
	100	6	86	82-91
	200	6	93	90-96
	500	6	98	91-101
Whole Ears	50	3	87	80-100
	200	3	89	86-90
	500	3	94	90-102

¹ From Table 2, Du Pont Study No. AMR-431-85

Du Pont Report No. AMR 1227-88 by J. E. Hall and J. E. Berry was used to determine DPX-M6316 in processed fractions (corn meal and corn oil). The results of these analyses is reported in Du Pont Report No. AMR 1128-88. The method is based upon a previous liquid chromatographic method for DPX-V9360 in corn forage, silage, grain and stover (Du Pont Report No. AMR-1260, 1988 by J. H. Larochelle, L. J. Major, and R. D. McFetridge). The current method uses two HPLC systems, one for cleanup and one for quantitation of the residue. The initial extraction of the corn meal sample is soaking 15 to 30 minutes in 20% methanol/80% pH 8 phosphate buffer solution, followed by grinding for 1 minute in Tisumizer, soak for additional 5 minutes, grind again for 1 minute, soak for 30 minutes, and then repeat the above grinding soaking steps. After centrifugation, the supernatant is reserved for further analysis. (Storage of samples at -20°C may occur at this

- 8 -

point for intervals of 1 to 5 days. Storage is supported by validation studies with good recoveries, see below).

A 10 gram sample of corn oil is dissolved in 100 ml of hexane, and shaken with 100 ml. of the 20% methanol/80% pH 8 phosphate buffer solution for 1 minute. The shaken solution is allowed to separate for 30 to 60 minutes. The supernatant organic layer is discarded and the underlying aqueous solution is retained for further analysis. (Storage of sample may occur at this point also. Data supporting storage intervals are included below).

Both samples of corn meal and corn oil are acidified to pH 2.5-3.5 with concentrated phosphoric acid and allow precipitate to form for 15 minutes before centrifugation. The 5 ml aliquot of the supernatant from centrifugation is then available for cleanup in the first liquid chromatograph (Waters Model #510 with Waters Model #PRO-380 controller) with Zorbax® Phenyl column using eluent of 43% methanol buffered to pH 3.0. The collected effluent is acidified with one drop of phosphoric acid and brought to volume (15 ml).

Quantitation by the analytical HPLC (another Waters Model #510) with Zorbax® R_x[™] column. The eluent is 20% methanol at pH 7.5 (phosphate buffer). Detection of DPX-M6316 residue is by Waters Model #481 spectrophotometer and is measured in terms of peak height or peak area.

The petitioner claims that the above method is very specific and free of interference. If interference is found, the pH of the eluent may be adjusted by 0.25 pH units to increase the retention time of DPX-M6316 about 2 minutes, to isolate away from the interference. Most commercial sulfonylurea herbicides would be detectable with this equipment and technique.

Recovery ¹ of DPX-M6316 by Du Pont Method AMR 1227-88 from processed corn meal and purchased corn oil ²					
Substrate	Fortification	Recovery			Average
Corn meal	0.02	135	110	95	
	0.05	102	114	82	
	0.10	110	82	85	
	0.2	116	97	92	101.7
Corn oil	0.02	105	115	100	
	0.05	88	86	72	
	0.1	87	83	77	
	0.2	98	97	81	90.8

¹ Includes 1-5 days sample storage @ -20°C during analysis.

² From Table I, Report No. AMR 1227-88

Conclusions:

- 9 -

The method of Du Pont Study No. AMR 431-85 Revision 3 August 11, 1988 is suitable for analysis of the parent compound thifensulfuron methyl in corn kernels, whole ears and corn forage. The limit of detection appears to be 0.02 ppm. The method of Du Pont Report No. AMR 1227-88 is suitable for the analysis of the parent compound thifensulfuron methyl in processed corn meal and processed corn oil. The lower limit of detection appears to be 0.02 ppm. A successful method trial of Du Pont Method AMR 235-84 (wheat or barley grain and straw) was conducted in conjunction with PP6F3431 (12/27/87, C. Deyrup). Method AMR 431-85 is sufficiently similar to Method AMR 235-84.

Storage Stability

Frozen storage stability studies for corn grain and corn forage indicate >90% recovery at fortification levels of 0.1 ppm (forage: range 85%-119% and grain: range 80%-113%) of thifensulfuron methyl at 24 months. The storage stability samples were lost due to fire after 24 months. The freezer storage intervals (i.e. the period of time between harvest and analysis of a sample) of some samples exceeded the duration of the reported storage stability study by approximately 7 months. However, since the stability of DPX-M6316 through 24 months shows no significant decline of residue levels, we are willing to conclude that thifensulfuron methyl will continue to be stable during an additional 7 months of freezer storage. The petitioner also submits freezer storage stability data for thifensulfuron methyl on wheat grain stored for 42 months. No significant loss of DPX-M6316 is shown (range of recovery at 0.1 ppm was 81% to 97%). Based upon freezer storage stability study of residues of thifensulfuron methyl in corn grain and further supported by the reported storage stability study in wheat grain, we conclude that freezer storage stability has not adversely affected the integrity of the submitted residue data.

Residue Data

The study of residue of thifensulfuron methyl in corn grain, forage and fodder has been submitted by the petitioner in Du Pont Study No. AMR-1233-88 "THE MAGNITUDE OF THE RESIDUES ON GRAIN, FORAGE, AND FODDER FROM CORN AFTER TREATMENT WITH DU PONT M6316 25DF HERBICIDE", by S. Mark Kennedy, July 6, 1988. Two laboratories were utilized for residue analysis: Du Pont Agricultural Products Department, Research and Development Division Experimental Station, Wilmington Delaware, 19898 and Wastex Industries, Inc. 28 Hanover Street, Pottstown, Pennsylvania 19464.

Field trials for corn grain in 15 locations across the US, while 11 sites were studied for residues in corn forage and fodder each. The states include CA, DE, IL-85, IL-87, IN, IA, LA, MI, NB, NC-86, NC-87, OH, SD, TX, and VA. These states are reported to account for 72% of the 1985 corn crop. The field trials were conducted in 1985, 1986, and

- 10 -

1987. Field applications of the 25DF were made by ground equipment and included exaggerated rates up to four times (actually 16x recommended rate; see note under Directions for Use) the maximum recommended rate at the proper plant growth stage specified on the proposed label. Application rates of thifensulfuron methyl as active ingredient ranged from 0.057 oz a.i./A. to 1.0 oz. a.i./A. Field spray solutions ranged from 10.1 gal per acre to 45.5 gal per acre. Samples of forage (entire aerial portion of immature plant), fodder (leaves and stalk of mature plant) and field corn grain. Kernels were separated from mature ears, however samples were of the entire ear. The contract laboratory Wastex, Inc., used the term 'forage' to indicate both immature and mature leaves and stalks. The petitioner has clarified the distinction in the data tables.

The analytical method AMR-431-85 Revision 1 (discussed above) is the method used by the petitioner to determine field residues of thifensulfuron methyl in corn forage, fodder and grain. Both Wastex, inc. and Du Pont used this method for thifensulfuron methyl. Wastex, Inc. labs showed recovery of thifensulfuron methyl in corn grain averaged 84% (range 73%-107%) at fortification levels of 0.02 ppm in and in corn forage/fodder 87% (range 71%-112%) at fortification levels of 0.05 ppm. Du Pont labs showed recovery of thifensulfuron methyl in corn grain averaged 87% (range 79%-90%) at fortification levels of 0.02 - 0.04 ppm.

For radiovalidation of the analytical method for weathered residues, corn forage from the corn metabolism study was analyzed by method AMR 435-85 Revision 1 to determine the efficiency of extraction of weathered DPX-M6316 residues. Both methods showed 0.078 ppm of DPX-M6316 in corn forage. Thus, the petitioner concludes that method AMR 435-85 revision 1 is 100% effective in extracting weathered DPX-M6316 residues from corn forage.

Residue decline trials were conducted in IL-87 and NC-87 conducted at 0.5 or 1.0 oz. a.i./A showed that residues of thifensulfuron methyl declined [from 7 ppm (IL-87) and 4 ppm (NC-87) both at exaggerated 1 oz. a.i./A.] to non-detectable levels (<0.05 ppm) in corn forage at all intervals greater than 14 days post treatment. The NC-87 trial employed surfactant in the field treatment while the IL-87 did not have surfactant; this may help explain the lower values found in NC field trial.

In regards to fodder and grain in the two residue decline studies (IL-87 and NC-87), no detectable residues (<0.05 ppm) of thifensulfuron methyl was detected in fodder or grain at 114 days (IL) or 165 days (NC). Samples in these decline studies were maintained under frozen storage for intervals up to 267 days post harvest. These intervals are well within validated frozen storage intervals discussed elsewhere in this review and in other reviews of this same chemical.

The other 16 studies were harvest residue trials, not residue decline studies. Samples of forage, fodder or grain were harvested at appropriate intervals. Forage samples were collected at 36, 44, 47, 48, 52, 52, 55, 56, 58, 73, or 97 days post treatment. Fodder samples were collected at 48, 91, 95, 102, 122, 126, 127, 135, 137, and 154 days after

- 11 -

treatment. Grain samples were collected on days 48, 80, 95, 100, 102, 117, 117, 126, 127, 127, 135, 137, 139, and 154 after treatment. All grain samples (harvested at 48 or more days after application) had nondetectable levels (<0.02 ppm) of thifensulfuron methyl. Similarly, all forage or fodder samples collected at 48 or more days had nondetectable levels (<0.05 ppm) of thifensulfuron methyl.

We conclude that residues of thifensulfuron methyl are not likely to exceed the proposed tolerances of 0.02 ppm in corn grain and 0.05 ppm in corn forage and corn fodder, when used in a single application at no more than 0.25 oz a.i/A. with a preharvest interval of 30 days prior to harvest of corn forage or fodder.

Residue Decline Studies Table 1											
Location	Use Rate (oz. ai/A)	Surfa ctant	Date Planted	Date Treated	Date Sample	Date Analyzed	PHI (days)	Days Storag e	DPX-M6316 Residue (ppm)		
									Forage	Fodder	Grain
Rochelle, Illinois @ 27.8 gals per acre Frozen	0.5		04/30/87	05/27/87	05/27/87	01/15/88	0	233	2.94		
	1								6.96		
	Check								<0.05		
	0.5				05/28/87	01/15/88	1	232	0.71		
	1								3.14		
	Check								0.05		
	0.5				05/30/87	01/15/88	3	230	0.46		
	1								0.65		
	Check								<0.05		
	0.5				06/03/87	01/15/88	7	226	0.08		
	1								0.06		
	Check								<0.05		
	0.5				06/10/87	01/15/88	14	219	<0.05		
	1								<0.05		
	Check								<0.05		
	0.5				06/24/87	01/15/88	28	205	<0.05		
	1								<0.05		
	Check								<0.05		
	0.5				08/24/87	01/15/88	89	144	<0.05		
	1								<0.05		
	Check								<0.05		
	0.5				09/23/87	01/15/88	119	114		<0.05	<0.02
	1								<0.05	<0.02	
	Check								<0.05	<0.02	

- 12 -

Residue Decline Studies Table 1											
Location	Use Rate (oz. ai/A)	Surfa ctant	Date Planted	Date Treated	Date Sample	Date Analyzed	PHI (days)	Days Storag e	DPX-M6316 Residue (ppm)		
									Forage	Fodder	Grain
Fayetteville, North Carolina @ 24.77 gals per acre Frozen	0.5	S	04/10/87	05/07/87	05/07/87	01/29/88	0	267	1.35		
	1								3.96		
	Check								<0.05		
	0.5	S			05/08/87	01/29/88	1	266	0.93		
	1								2.04		
	Check								0.05		
	0.5	S			05/11/87	01/29/88	4	263	0.15		
	1								0.67		
	Check								<0.05		
Madera, CA @ 40 gal per acre Stored Frozen	0.5	S			05/14/87	01/29/88	7	260	<0.05		
	1								0.06		
	Check								<0.05		
	0.5	S			05/21/87	01/29/88	14	253	<0.05		
	1								<0.05		
	Check								<0.05		
	0.5	S			06/04/87	01/29/88	28	239	<0.05		
	1								<0.05		
	Check								<0.05		
Madera, CA @ 40 gal per acre Stored Frozen	0.5	S			07/17/87	01/29/88	71	196	<0.05		
	1								<0.05		
	Check								<0.05		
	0.5	S			08/17/87	01/29/88	102	165		<0.05	<0.02
	1									<0.05	<0.02
	Check									<0.05	<0.02
	0.25		04/23/87	05/12/87	08/17/87	01/18/88	97	154	<0.05		
	0.5								<0.05		
	0.5	S							<0.05		
Madera, CA @ 40 gal per acre Stored Frozen	1								<0.05		
	Check								<0.05		
	0.25				09/16/87			127			<0.02
	0.5										<0.02
	0.5	S									<0.02
	1										<0.02
	Check										<0.02
	0.25				09/11/87			122			<0.05
	0.5								<0.05		
Madera, CA @ 40 gal per acre Stored Frozen	0.5	S							<0.05		
	1								<0.05		
	Check								<0.05		

Location	Use Rate (oz. ai/A)	Surfa- ctant	Date Planted	Date Treated	Date Sample	Date Analyzed	PHI (days)	Days Storag- e	DPX-M6316 Residue (ppm)		
									Forage	Fodder	Grain
Farmington, MN @ 22.78 gal per acre Stored Frozen	0.11		05/10/85	06/05/85	07/30/85	09/18/87	55	780	<0.05		
	0.23								<0.05		
	0.45								<0.05		
	Check								<0.05		
	0.11		05/20/85	06/08/85		52	780	<0.05			
	0.23				<0.05						
	0.45				<0.05						
	Check				<0.05						
	0.11		05/20/85	06/24/85		36	780	<0.05			
	0.23				<0.05						
	0.45				<0.05						
	Check				<0.05						
Farmington, MN @ 22.78 gal per acre Stored Frozen	0.23		05/20/85	06/08/85	10/21/85	02/03/88	135	835		<0.05	<0.02
	0.45								<0.05	<0.02	
	Check							<0.05	<0.02		
Nevada, IA @ 30 gal per acre Stored Frozen	0.11		04/21/85	05/18/85	08/21/85	01/29/88	95	891		<0.05	<0.02
	0.23								<0.05	<0.02	
	0.45								<0.05	<0.02	
	Check								<0.05	<0.02	
Center Village, OH @ 20 gal per acre Stored 1 Day	0.25	S	05/31/85	07/03/85	08/20/85	02/03/88	48	897	<0.05		
	Check								<0.05		
	0.25	S								<0.05	<0.02
	Check							<0.05	<0.02		
Hazelwood, IN @ 26 gal per acre Stored 1 Day	0.45		05/16/85	06/03/85	11/04/85	02/23/88	154	841		<0.05	<0.02
	0.45								<0.05	<0.02	
	Check								<0.05	<0.02	
Fairbury IL. @ 24 gal per acre Stored Frozen	0.23		05/05/85	06/07/85	08/26/85	02/18/88	80	906			<0.02
	0.45										<0.02
	0.9										<0.02
	Check										<0.02
	0.23								05/05/85	06/07/85	07/24/85
0.45		<0.05									
0.9		<0.05									
Check		<0.05									
Newark, DE @ 20 gal per acre Stored Frozen	0.25	S	06/19/86	07/09/86	09/05/86	02/11/88	58	524	<0.05		
	0.5	S							<0.05		
	Check								<0.05		
Clinton, LA @ 15 gal per acre Forage Frozen Grain stored 1 day	0.25		03/29/86	04/28/86	06/11/86	02/03/88	44	602	<0.05		
	Check								<0.05		
	0.25								03/29/86	04/28/86	08/06/86
0.5		<0.02									

Location	Use Rate (oz. ai/A)	Surfa- ctant	Date Planted	Date Treated	Date Sample	Date Analyzed	PHI (days)	Days Storag- e	DPX-M6316 Residue (ppm)		
									Forage	Fodder	Grain
Hart, TX @ 15 gal per acre Forage Frozen Grain & fodder stored 1 day	0.23 0.45 0.9 Check		04/17/85	05/24/85	09/03/85	02/18/88	102	898	<0.05 <0.05 <0.05 <0.05	<0.02 <0.02 <0.02 <0.02	
	0.23 0.45 0.9 Check		04/17/85	05/24/85	08/05/85	02/18/88	73	927	<0.05 <0.05 <0.05 <0.05		
Elk Point, SD @ 15 gal per acre Forage Frozen	0.25 0.5 0.75 1 Check	S S S S	05/05/85	06/03/85	07/25/85	02/11/88	52	931	<0.05 <0.05 <0.05 <0.05 <0.05		
Edinburg, VA @ 45.5 gal per acre Forage Frozen	0.25 0.45 0.9 Check		04/25/85	05/24/85	08/23/85	02/23/88	91	914	<0.05 <0.05 <0.05 <0.05		
	0.25 0.45 0.9 Check	S S S	04/25/85	05/24/85	09/18/85	02/23/88	117	888		<0.02 <0.02 <0.02 <0.02	
Oakland, NE @ 20 gal per acre Forage Frozen	0.23 0.45 0.9 Check		05/09/85	05/28/85	07/23/85	02/23/88	56	945	<0.05 <0.05 <0.05 <0.05		
	0.23 0.45 0.9 Check		05/09/85	05/28/85	10/12/85	02/23/88	137	864	<0.05 <0.05 <0.05 <0.05	<0.02 <0.02 <0.02 <0.02	
Fayetteville, NC @ 25 gal per acre Forage Frozen	0.11 0.23 0.45		04/14/86	05/06/86	09/10/86	10/26/87	127	411	<0.05 <0.05 <0.05	<0.02 <0.02 <0.02	
	0.23 0.45 Check	S S	04/14/86	05/12/86	09/15/86	10/26/87	126	406	<0.05 <0.05 <0.05	<0.02 <0.02 <0.02	
Rosemount, MN @ 10.1 gal per acre Forage Frozen	0.9 Check	S	04/30/87	05/23/87	10/09/87	02/16/88	139	130		<0.02 <0.02	
Newark, DE @ 24 gal per acre Forage Frozen	0.057 0.11 0.23 Check	S S S	05/01/85	05/24/85	09/18/85	02/20/86	117	155		<0.02 <0.02 <0.02 <0.02	

- 15 -

Processed Commodities:

The study of thifensulfuron methyl residues in processed commodities is Du Pont Study No. AMR-1128-88 "MAGNITUDE OF DPX-M6316 HERBICIDE RESIDUES IN CORN AND PROCESSED PRODUCTS AFTER APPLICATION OF DPX-M6316", by James E. Hall and James E. Berry, November 10, 1989. The analytical method is "Method Of Analysis For DPX-M6316 In Corn Processed Fractions By Liquid Chromatography" AMR- 1227-88 by J. E. Hall and J. E. Berry. (See Analytical Method above for discussion of method and validation data).

Test plots at Oregon, Missouri were treated at 0.5, 1.0 and 2.0 oz. a.i./A., which the report claims to be 2x, 4x and 8x the maximum recommended label use rate. However, the maximum recommended use rate in Section B, page 2, of PP0F3872 indicates a maximum of 0.0625 oz a.i./A., based upon 0.25 oz. Pinnacle® per acre * 25% active ingredient = 0.0625 oz. a.i./A. [Note that field residue trials were generally run at 0.25 oz a.i./A. or more]. Accordingly, using the currently proposed maximum, the these field trials actually constitute exaggeration rates of 8x, 16x, and 32x, respectively.

Field corn grain samples were obtained for processing by 'nonsystematic' sampling. Grain was ground with dry ice in a blender to produce a powder. A 500 g. sample of the powder was extracted 6 times with 2 liters of hexane at 63°C for thirty minutes. The hexane was evaporated to dryness, leaving the extracted corn oil. The extracted ground corn meal was allowed to dry. The petitioner contends that these practices are equivalent to 'dry milling' of corn grain. Method AMR- 1227-88 was used to analyze residues of DPX-M6316.

There were no detectable residues (<0.02 ppm) of thifensulfuron methyl in unprocessed corn grain treated with up to 2 oz. a.i./A. and used for processing. The analysis of the processed corn oil and the corn meal also showed no detectable residues (<0.02 ppm) of thifensulfuron methyl in either oil or meal.

Based upon these exaggerated dosage studies, we conclude that residues of thifensulfuron methyl are not likely to concentrate in corn milling fractions and therefore, food additive tolerances are not required at this time.

Meat, Milk, Poultry, and Eggs

The animal feed items of concern herein are corn grain and corn forage and fodder. Corn grain can used up to 80% of the beef diet, 50% of the dairy cattle diet, 70% of the poultry diet and 85% of the swine diet. Corn forage and fodder may be used up to 25% each in beef cattle and 10% in dairy cattle. Corn forage and fodder are not used for other livestock. Using a cattle diet of 25% forage or fodder at 0.05 ppm and 75% corn grain at 0.02 ppm, the dietary burden would be about 0.03 ppm.

- 16 -

Residue data discussed above showed no detectable residue (<0.02 ppm) of thifensulfuron methyl in corn grain from exaggerated application rate up to 16X assuming that the labeled rate of 0.0625 oz. active /acre is correct and no detectable residue (<0.05 ppm) of thifensulfuron methyl in corn forage or fodder 30 days after application.

As in the previous petition (PP6F3431) for this chemical, in the light of the goat metabolism study showing 'minimal' transfer of DPX-M6316 residues to meat and milk at 2800x feeding levels and in the absence of detectable residues in animal feed items corn grain, forage or fodder, we are not requiring tolerances for meat, milk, poultry or eggs at this time. If the petitioner should propose a future use which results in detectable residues in animal feed items, feeding studies and tolerances may be required for secondary residues in meat, milk, poultry, and eggs.

Other Considerations

International Residue Limits

An International Residue Limit Status Sheet (Codex) is attached to our review.

Attachment: IRLS (Codex)

cc: PM25, Cook, PP0F3872 ,RF,Circ(7),PIB/FOD(Furrow)
H7509C:CBTS:Rcook:rc:x77484:Rm810H:4/21/92
RDI:R.S.Quick:4/21/92:R.Loranger:4/21/92

F. Hest
6/19/91

<u>INTERNATIONAL RESIDUE LIMIT STATUS</u>			
Chemical: thifensulfuron methyl (DPX-M6316; Pinnacle; Harmony)			
Codex No:			
<u>Codex Status:</u>		<u>Proposed U. S. Tolerance</u>	
<input checked="" type="checkbox"/> No Codex Proposal Step 6 or Above		Petition No: PP0F3872	
		DEB Reviewer: R. W. Cook	
Residue (if Step 8):		Residue thifensulfuron methyl <u>per se</u> per 40 CFR 180.439	
Crop(s)	Limit (mg/kg)	Crop(s)	Limit (mg/kg)
		Corn grain, field Corn forage, field Corn fodder, field	0.02 0.05 0.05
<u>Canadian limits:</u>		<u>Mexican Limits</u>	
<input checked="" type="checkbox"/> No Canadian limit <i>on above</i>		<input checked="" type="checkbox"/> No Mexican limit	
Residue		Residue	
Crop(s)	Limit (mg/kg)	Crop(s)	Limit (mg/kg)
Notes: No food additive tolerance. No feed additive tolerance.		Page <u>1</u> of <u>1</u> . Form Revised 9/90	



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Chemical: Thifensulfuron methyl

PC Code: 128845

HED File Code 11000 Chemistry Reviews

Memo Date: 04/23/92

File ID: DPD156732

Accession Number: 412-03-0019

HED Records Reference Center
01/09/2003